REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	18 April. 96	technical; 01JUNE 95 to 30SEPT96

4. TITLE AND SUBTITLE

Polarization Dependent Recordings of Surface Relief Gratings on Azobenzene Containing Polymer Films

5. FUNDING NUMBERS

C: N00014-90-J-1148

R&T Code: 4132016

Dr. Kenneth J. Wynne

6. AUTHOR(S)

X.L. Jiang, L. Li, J. Kumar, D.Y. Kim, V. Shivshankar, S.K. Tripathy

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

University of Massachusetts Lowell
Department of Chemistry
1 University Avenue
Lowell, MA 01854

8. PERFORMING ORGANIZATION REPORT NUMBER

1148-95-04

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Office of Naval Research-Physical S&T Division, ONR 331
Department of the Navy
Arlington, Virginia 22217-5000

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION / AVAILABILITY STATEMENT

Reproduction in whole or in part is permitted for any purpose of the United States Government.
This document has been approved for public release and sale; its distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 Words)*

Experimental studies on the recording of surface relief gratings on azobenzene containing polymer films using laser beams with different polarizations were carried out. The results indicate that the localized variations of light intensity and alternation of the resultant electric field polarization in the film are essential to the formation of the surface relief gratings.

14. SUBJECT TERMS

surface relief gratings; diffraction efficiencies; polarization dependent recordings

15. NUMBER OF PAGES

13

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

OFFICE OF NAVAL RESEARCH

GRANT N00014-90-J-1148

R&T Code 4132016

Scientific Officer: Dr. Kenneth Wynne

Technical Report No. 95-04

Polarization Dependent Recordings of Surface Relief Gratings on Azobenzene Containing Polymer Films

by

X.L. Jiang, L. Li, J. Kumar, D.Y. Kim, V. Shivshankar, S.K. Tripathy

Submitted to

Applied Physics Letters

University of Massachusetts Lowell
Department of Chemistry
Lowell, Massachusetts

April 18, 1996

Polarization dependent recordings of surface relief gratings on azobenzene containing polymer films

X. L. Jiang, L. Li, and J. Kumar
Center for Advanced Materials, Department of Physics
University of Massachusetts Lowell, Lowell, MA 01854

D. Y. Kim, V. Shivshankar, and S. K. Tripathy
Center for Advanced Materials, Department of Chemistry,
University of Massachusetts Lowell, Lowell, MA 01854

Experimental studies on the recording of surface relief gratings on azobenzene containing polymer films using laser beams with different polarizations were carried out. The results indicate that the localized variations of light intensity and alternation of the resultant electric field polarization in the film are essential to the formation of the surface relief gratings.

Submitted to:
Applied Physics
Letters. 1996

Over the past decade, photoinduced orientation of azobenzene groups due to trans-cis-trans isomerization has been widely used for producing refractive index gratings and birefringence gratings (orientation gratings) in azobenzene containing polymers.[1-5] It was recently reported that surface relief gratings could be directly recorded on azobenzene containing polymer films using Ar^+ laser beams.[6-8] The formation of large surface modulation on the polymer films could be attributed to the polymer chain migration.[6-8] During recordings, two distinct processes, the formations of birefringence grating and surface relief grating, were observed. Local motion connected with the photoinduced trans-cis-trans isomerization and a localized thermal effect due to absorption of light were suggested to be the mechanism on the formation of the surface relief gratings.[8] It is known that linearly polarized light could induce an orientation of azobenzene groups in the direction perpendicular to the polarization of light.[1-5,8-10] The polarization dependent recordings of refractive index gratings and birefringence gratings have been extensively studied. The diffraction efficiencies of refractive index and birefringence gratings induced by two laser beams with orthogonal polarization (polarization recording) and with parallel polarization (intensity recording) behaved very differently.[1-3] Very recently, we have observed that two *p*-polarized recording beams induced much larger surface relief structures than two *s*-polarized recording beams.[8] This letter reports the detailed studies on the polarization dependent recordings of the surface relief gratings.

An azobenzene containing epoxy-based polymer was used for the study. It was synthesized from diglycidyl ether of bisphenol A and 4-(4'-nitrophenylazo) phenyl amine.[11,12] Its glass transition temperature is 115°C. The characterization of the optical properties of this polymer has been described elsewhere.[12] The polymer was dissolved in propylene glycol methyl ether acetate and 1,4-dioxane (volume ratio 3:1) with a weight ratio of 1:10. The

solution was spin-coated on glass slides and then baked at 70°C under vacuum for 12 hours. The typical film thickness was about 0.8 μm.

The experimental setup for the grating recording is shown in Fig. 1. A linearly polarized laser beam at 488 nm from an Ar^+ laser is used. The polarized laser beam passes through an halfwave plate, and is then expanded and collimated. Half of the collimated beam passes through another halfwave plate and is incident on the sample directly. The other portion of the beam is reflected onto the sample from an aluminum coated mirror. Two sets of experiments were carried out. In the first set of experiments, the second halfwave plate was not in position. Laser beams with different polarizations (defined by an angle α, with respect to s-polarization) was achieved by rotating the first halfwave plate. By replacing this halfwave plate with a quarter wave plate or a depolarizer, circularly polarized and unpolarized recording beams were obtained respectively. Due to the complex refractive index of aluminum, the polarization of the beam reflected from the mirror becomes elliptically polarized except for $\alpha=0°$ (s-polarization) and $\alpha=90°$ (p-polarization). In the second set of experiments, by selecting either $\alpha=0°$ or $\alpha=90°$ and positioning the second halfwave plate in one of the recording beams as mentioned earlier, two orthogonally polarized recording beams (polarization recording) could be obtained. The typical intensity of the recording beam after the collimating lens was 55 mW/cm^2 and the recording time was about 45 minutes. The incident angle θ of the recording beams was selected to be 14°, resulting in grating spacing of about 1 μm. The diffraction efficiency of the first order diffracted beam from the gratings in transmission mode was probed with an unpolarized low power He-Ne laser, which was used to monitor the grating formation process.

The diffraction efficiencies and surface modulations of the gratings recorded under different recording conditions are summarized in Table I. All

the diffraction efficiency values in the table were measured at least one day after the gratings were recorded to ensure that there are no transient effects involved. The surface modulations of the gratings were studied by an atomic force microscope (AFM).

Due to the superposition of two recording beams with different polarizations, there exist certain distributions of the resultant electric field in the film. The resultant electric field vector varies spatially and periodically in both magnitude and direction. It should be noted that since one recording beam is reflected from an aluminum coated mirror, the reflectivity of electric field is a complex number and it makes the distribution of the resultant electric filed more complicated except for the recording conditions with either s- or p-polarized beams.

Under the condition for intensity recording ($\alpha=0^{\circ}$), interference of the two recording beams with parallel polarization will give rise to the largest light intensity variation. However, the resultant electric field is always linearly polarized and in the same direction over the entire irradiated area (i.e., there is no spatial alternation of the resultant electric field polarization). Very low diffraction efficiency and small surface modulation (<100 Å) were obtained from the grating recorded. The diffraction efficiency as a function of time during the recording process is shown in Fig. 2. The rapid increase of the diffraction efficiency at the initial stage is due to the formation of refractive index grating created by photoinduced orientation. From the maximum diffraction efficiency, a change in refractive index was estimated to be 0.02. The efficiency then dropped to a very small value and remained at that value throughout the rest of the recording process. This drop could be attributed to the cancellation of the refractive index grating by small surface modulation.

Under the polarization recording condition, the greatest alternation of the

resultant electric field polarization on the film surface resulting from the superposition of the field of the two recording beams with orthogonal polarization occurs. However, the light intensity on the film is uniform over the entire irradiated area. Very small surface modulation and diffraction efficiency were also obtained under this recording condition. Fig. 3 shows the diffraction efficiency as a function of time during the recording process. As the orientation grating formed, the diffraction efficiency increased, saturated and remained at a constant value throughout the rest of the recording process. After the laser beams were switched off, the diffraction efficiency decayed nearly to zero, indicating that most of the orientation grating had been erased.

Under the other recording conditions, which could be termed mixed recording conditions, variations of both light intensity and the resultant electric field polarization on the film exist. Surface relief gratings could be formed, leading to much greater values of diffraction efficiency and surface modulation than those from intensity recording as well as from polarization recording. This seems to indicate that the existence of both light intensity and resultant electric field polarization variations is essential to the formation of surface relief gratings. It is expected that by choosing certain polarization of the recording beams, maximum diffraction efficiency and surface modulation could be achieved. Under the recording condition of α=45°, a very large diffraction efficiency of 27% and the maximum surface modulation of 3600 Å were obtained. A typical grating formation process of mixed recording as probed by the diffraction efficiency is shown in Fig. 4. The photoinduced orientation effects leading to refractive index and orientation gratings contributed to the initial increase of the diffraction efficiency. It is experimentally verified by the observation of AFM that in the first minute of recording, the surface relief gratings are not formed. The following stage might involve the saturation of

orientation grating and partial cancellation of the refractive index grating by the surface modulation. In the later stage, the diffraction efficiency increased almost linearly until saturation. We therefore infer that the increase of diffraction efficiency after the first minute or so of recording indicates the formation process of the surface relief grating. The gratings recorded with circularly polarized and unpolarized laser beams also revealed large surface modulations with high diffraction efficiencies.

In conclusion, we have observed that the formation of surface relief gratings on the azobenzene containing polymer films strongly depends on the polarization of the recording beams. Very large surface modulation could be achieved by controlling the polarization of recording beams. Although the exact driving force of the migration of the polymer chains is not well understood, we believe that the existence of the spatial variations of both magnitude and direction of the resultant electric field vector in the films is an essential condition to induce surface modulations. The results of polarization dependent experiments clearly imply that spatial variation thermal effects due to light absorption is not sufficient to record the large surface relief gratings. We have earlier established [13] that the polymers containing the chromophores which can not participate in the tans-cis-trans isomerization do not give rise to appreciable surface relief gratings. We therefore speculate that the macroscopic motion of polymer chains is due to the interaction of the dipoles with internally generated fields, as chromophores are continuously cycled through the trans-cis-trans isomerization.

Financial support from ONR and NSF-DMR is gratefully acknowledged.

1 T. Todrov, L. Nikolova, N. Tomova, and V. Dragostinova, Appl. Opt. **23**, 4588 (1984).

2 T. Todrov, L. Nikolova, N. Tomova, and V. Dragostinova, IEEE J. Quant. Elet. QE-**22**, 1262 (1885).

3 Jean J. A. Couture and Roger A. Lessard, Appl. Opt. **27**, 3368 (1988).

4 P. Rochon, J. Gosselin, A. Natansohn, and S. Xie, Appl. Phys. Lett. **60**, 4 (1992).

5 A. Natansohn, P. Rochon, J. Gosselin, and S. Xie, Macromolecules, **25,** 2268 (1992).

6 P. Rochon, E. Batalla, and A. Natansohn, Appl. Phys. Lett. **66**, 136 (1995).

7 D. Y. Kim, L. Li, J. Kumar, and S. K. Tripathy, Appl. Phys. Lett. **66**, 1166 (1995).

8 D. Y. Kim, L. Li, X. L. Jiang, V. Shivshankar, J. Kumar, and S. K. Tripathy, Macromolecules **28,** 8835 (1995).

9 C. Jones and S. Day, Nature, **351**, 15 (1991).

10 K. Anderle, R. Birenheide, M. J. A. Werner, and J. H. Wendorff, Liq. Cryst. **9**, 691 (1991).

11 B. Mandal, R. Jeng, J. Kumar, and S. K. Tripathy, Makromol. Chem., Rapid Commun. **123**, 607 (1991).

12 Yong Ming Chen, Ru Jong Jeng, Lian Li, Xiaofan Zhu, Jayant Kumar, and Sukant Tripathy, Mol. cryst. Liq. cryst. Sci. Techinol - Sec. B: Nonlinear Optcis, **4**, 71 (1993).

13 D. Y. Kim, J. Kumar, and S. K. Tripathy, PMSE Proceedings, **73**, 477 (1995).

Table I. The diffraction efficiencies and surface modulations under different recording conditions

Recording conditions	Diffraction efficiency (%)	Surface modulation (Å)
$\alpha=0^\circ$	<0.01	<100
$\alpha=8^\circ$	0.4	250
$\alpha=16^\circ$	5.5	1470
$\alpha=24^\circ$	15	2140
$\alpha=45^\circ$	27	3600
$\alpha=65^\circ$	17	2770
$\alpha=90^\circ$	15.2	2540
Unpolarized	16.5	2560
Circularly polarized	30	3500
Polarization recording	<0.05	<100

Figure Captions

Fig. 1 Experiment setup for the grating recording by laser beam with different polarizations.

Fig. 2 Diffraction efficiency as a function of time under the intensity recording condition.

Fig. 3 Diffraction efficiency as a function of time under the polarization recording condition.

Fig. 4 Diffraction efficiency as a function of time under a mixed recording condition (α=45°). The inset shows the initial stages of the grating formation (about 90 seconds).

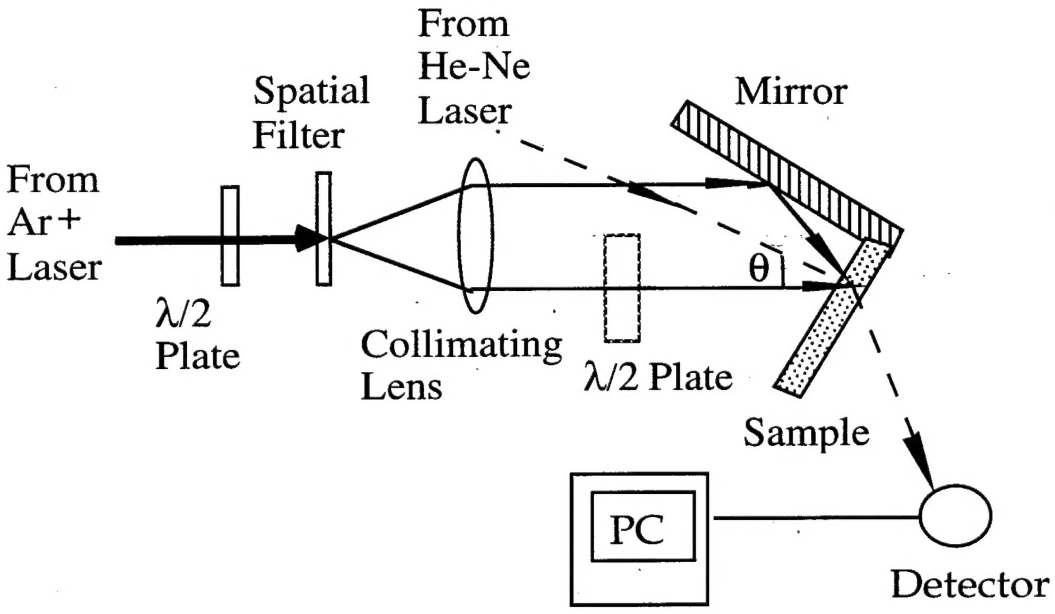

Fig. 1, X. L. Jiang, Appl. Phy. Lett.

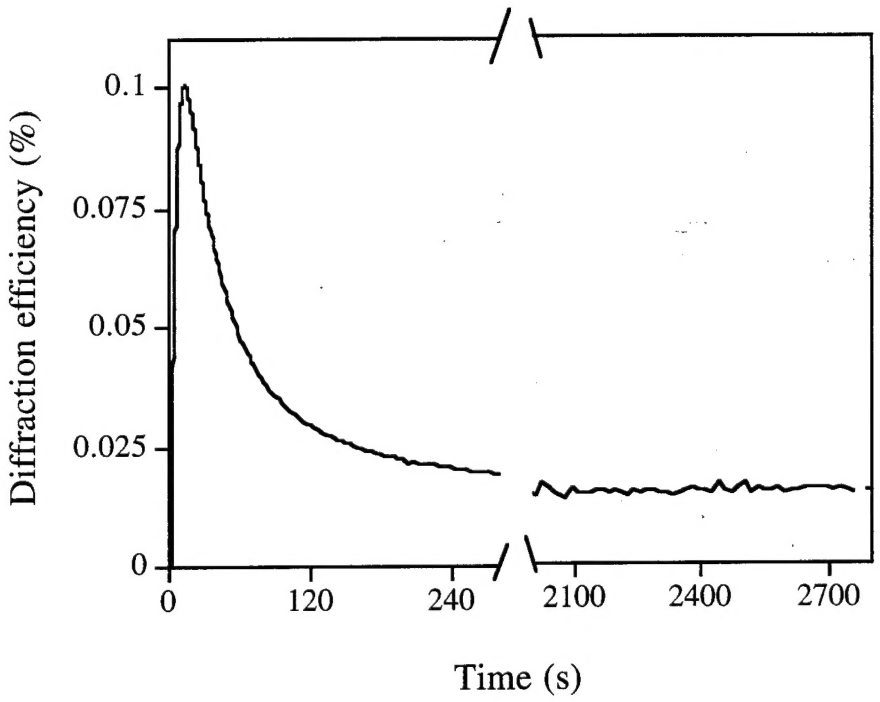

Fig. 2, X.L. Jiang, Appl. Phy. Lett.

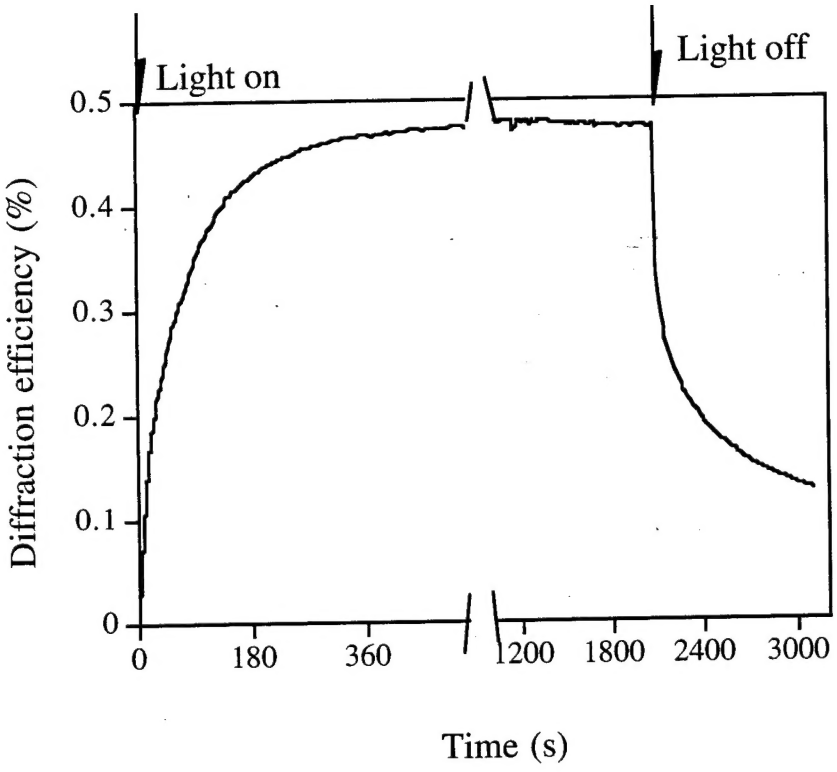

Fig. 3, X.L. Jiang, Appl. Phy. Lett.

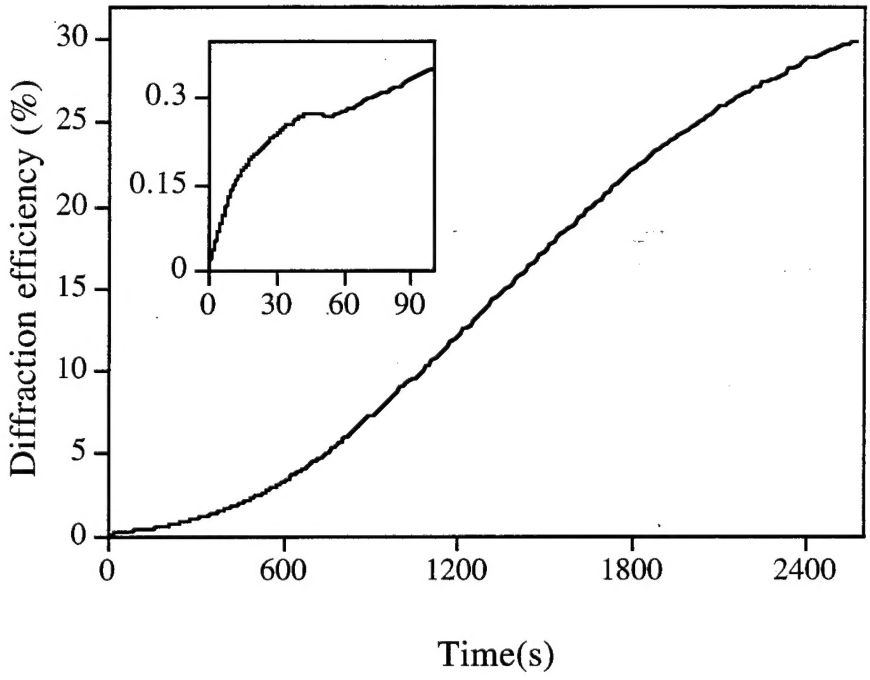

Fig. 4, X.L. Jiang, Appl. Phy. Lett.